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A STUDY OF PHYSICOCHEMICAL PROCESSES WHEN PELLETIZING SINTERING MIXTURE

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Abstract

Data on the physico-chemical processes occurring during the pelletization of sintering mixture were obtained by bench and laboratory studies. Both the sintering parameters of the mixture and the intensity of dust and harmful gases entry into the atmospheric air together with sintering gases depend on the degree and quality of pelletization. The adsorption of surfactants was studied; the adhesion of surfactant solutions was calculated on the basis of contact angle measurements; an original method was applied for measuring the rupture force used for breaking the wetted sintering mixture, and data on the change in the fractional composition of the sintering mixture after the wetting were obtained. The optimal parameters of the pelletizing process were established. The optimal concentration of surfactant (TEAS) in the pelletizing solution was 0.00015 – 0.00020 mol/l at a flow rate of 70 – 80 g per ton of the sintering mixture; the best wetting and the smallest dust content (the percentage of sintering mixture fractions <3 mm) is provided by using seawater as a solvent. It is noted that not only a decrease, but also an increase in the TEAS concentration relative to the optimal value leads to a noticeable deterioration in the sintering mixture quality. Presumably, this behavior of the system under study is associated with both the size effects and the increased polarization of the sulfo group in the surfactant.
Key words: surfactants; adhesion; wetting; dustiness; fractional composition

ДОСЛІДЖЕННЯ ФІЗИКО-ХІМІЧНИХ ПРОЦЕСІВ ПРИ ОҐРУДКУВАННІ АГЛОШИХТИ

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Анотація

За допомогою стендових та лабораторних випробувань отримані відомості про фізико-хімічні процеси, які відбуваються при оґрудкуванні аглошихти. Від ступеня та якості окомкування залежать як параметри спікання шихти, так і інтенсивність переходу у навколишнє середовище аглогазів, які містять пил та шкідливі компоненти. Була вивчена адсорбція поверхнево-активних речовин (ПАР); за даними вимірювань крайових кутів змочування розрахована адгезія розчинів ПАР; за оригінальною методикою виміряна сила, що витрачається на розривання змоченої аглошихти, а також отримані дані про змінення фракційного складу аглошихти після змочування. Визначені оптимальні параметри процеса окомкування. Оптимальна концентрація ПАР (ТЕАС) у розчині для окомкування склала 0.00015 – 0.00020 моль/л при витратах 70 – 80 г на тону аглошихти; найкраще змочування та найменший вміст пилу (частка фракцій аглошихти < 3 мм) спостерігається при застосуванні морської води в якості розчинника. Відзначено, що не тільки зниження, а й збільшення концентрації ТЕАС відносно оптимального значення приводить до помітного погіршення якості аглошихти. Вірогідно, така поведінка досліджуваної системи пов'язано як із розмірними ефектами, так і з посиленням поляризації сульфогрупи у складі поверхнево-активної речовини.
Ключові слова: поверхностно-активні речовини; адгезія; змочування; запиленість; фракційний склад.

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ИССЛЕДОВАНИЕ ФИЗИКО-ХИМИЧЕСКИХ ПРОЦЕССОВ ПРИ ОКОМКОВАНИИ АГЛОШИХТЫ

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Аннотация

С помощью стендовых и лабораторных исследований получены данные о физико-химических процессах, протекающих при окомковании аглошихты. От степени и качества окомкования зависят как параметры спекания шихты, так и интенсивность поступления в атмосферный воздух с аглогазами пыли и вредных газов. Была изучена адсорбция поверхностно-активных веществ (ПАВ); на основании измерений краевого угла смачивания рассчитана адгезия растворов ПАВ; по оригинальной методике измерена сила, пошедшая на разрыв смоченной аглошихты, а также получены данные об изменении фракционного состава аглошихты после смачивания. Установлены оптимальные параметры процесса окомкования. Оптимальная концентрация ПАР (ТЭАС) в растворе для окомкования составила 0.00015 – 0.00020 моль/л при расходе 70 – 80 г на тонну аглошихты; наилучшее смачивание и наименьшее содержание пыли (доля фракций аглошихты < 3 мм) обеспечивается при использовании морской воды в качестве растворителя. Отмечено, что не только снижение, но и увеличение концентрации ТЭАС относительно оптимального значения приводит к заметному ухудшению качества аглошихты. Предположительно, такое поведение исследуемой системы связано как с размерными эффектами, так и с усилением поляризации сульфогруппы в составе поверхностно-активного вещества.

Ключевые слова: поверхностно-активные вещества; адгезия; смачивание; запыленность; фракционный состав.

Introduction

The optimization of many technological processes and increasing their technical and economic efficiency depend on the use of the results of scientific achievements in the study of physicochemical phenomena taking place in complex multiphase systems. These phenomena include sintering processes at metallurgical plants. In sinter obtaining processes an important place is occupied by the pelletization of the mixture before its sintering on sinter machines. Both the required sintering parameters and the intensity of the admission of dust and harmful gases to the atmospheric air with sintering gases depend on the degree and quality of pelletization, which is the main reason for the extremely difficult environmental situation in the areas of metallurgical enterprises operation.

The pelletization of the sintering mixture is a complex physicochemical process. Its parameters depend on the mineralogical composition of the mixture, its dispersion composition, humidity, degree of the hydrophilization of the particles surface. For pelletizing the mixture, water is added. The experience of many sinter plants shows that its use does not always provide the required degree of pelletization. First of all, this concerns the fine fractions of the sintering mixture, the presence of which in the charge leads to the deterioration of the sintering process itself, and also causes the emission of dust particles into the waste gas ducts of the sintering plants [1–12].

In recent years, to improve pelletizing and optimize sintering, surface-active substances (surfactant) have been put to use [8; 10; 13; 14]. It is shown that the use of surfactants as wetting additives improves the quality of the obtained agglomerate and reduces the content of dust and harmful gases in the waste sintering gases [9–11; 13–16].

For research in this work, we chose an anion active surfactant based on triethanolamine salts (TEAS). TEAS is a biologically mild surfactant, produced by industrial enterprises of Ukraine and other countries, and having a relatively low market value.

The aim of this work was to establish the physicochemical characteristics of surfactant solutions in the processes of their interaction with the surface of polydisperse solid phase and to develop on this basis the optimal processing parameters for bulk materials, allowing to improve the quality of sintering mixture in sinter production.

Experimental part

Research methods. The surface tension of surfactant solutions was determined by the maximum bubble pressure method using the Rebinder instrument [17; 18]. TEAS solutions were prepared by dissolving the appropriate amounts of the surfactant in distilled, tap and sea water. The latter was taken in the water area of the Azov Sea, since a number of metallurgical enterprises commonly using sea water for technological purposes are situated in that area. The concentration of surfactant was measured in the range from 0 to 5 wt. %. The research of the contact angle of these solutions was carried out by the capillary rise method.

To determine the effect of adhesion forces on the pelletizing processes in sintering mixture treated with surfactant solutions, we developed a laboratory Test bench, in which the adhesion work was evaluated by the amount of work expended on rupturing the compressed bulk material.

The basic ideas for the creation of this laboratory Test bench were outlined in the works of P. A. Kozlov and E. I. Andrianov [17; 18]. In this work we present the description of the Test bench and the principles of conducting research on it [16].

Sintering mixture samples were taken directly from the ore yard stack of the sinter department of ArcelorMittal Krivoy Rog metallurgical plant. The prepared samples were dried in a vacuum cabinet at a temperature of 110 °C to constant weight. Weighted portions were treated with surfactant solutions based on the specific consumption of 100 g / t, which corresponded to the sintering mixture moisture content of 10 % (standard total moisture adopted for the sintering mixture at sintering plants for pelletization). The concentration of surfactants in aqueous solutions ranged from 0.02 to 0.15 %, which corresponded to the specific consumption of surfactants from 20 to 150 g / t.

The evaluation of the efficiency of sintering mixture treatment with surfactant solutions was carried out on the laboratory Test bench of OJSC ArcelorMittal Krivoy Rog. The Test bench included a drum pelletizer, an installation for sieving the pelletized sintering mixture, an agglomerate sintering furnace, an installation for studying the parameters of the ready agglomerate. The sintering furnace is equipped with a mini-exhauster and a system for cleaning and removal of sintering gases.

All tests were carried out in accordance with the methods approved by the Ministry of Ukraine [19]. A 75 kg sintering mixture sample was loaded into the drum pelletizer, where it was mixed for 4 minutes without moistening, and then another 6 minutes after moistening. The total humidity of the sintering mixture in all cases was 8 ± 0.2%. For moistening surfactant solutions were taken (with concentrations from 0 to 0.01%, which corresponded to specific consumption from 0 to 100 g / t) made on tap water.

The granulometric composition of the pelletized sintering mixture (fractions larger than 12 mm, 8 – 5 mm, 5 – 3 mm, and < 3 mm) was determined on a sieve analyzer. A part of the pelletized sintering mixture weighing 35 kg, taken from the drum pelletizer, was loaded into the sintering furnace. While the mixture was sintering, dust samples of the sintering gases at the exit from the exgasator gas duct were taken by aspiration method using AFA filters.

To determine the effectiveness and feasibility of using surfactant solutions in the processing of sintering mixture, a set of pilot tests was performed. It included the development of the technological scheme, the treatment of the sintering mixture with TEAS solutions [13; 15; 16], the study of the sintering mixture dust content in the gas ducts of the sintering plant and at the exit to the atmosphere.

Results and its discussion

In the study of the surface tension of the surfactant aqueous solutions functional dependencies σ = f(C(TEAS)) were obtained. The results of these studies are given in [16; 20]. The form of the corresponding isotherms is typical for surfactant solutions, but the effect of the solvent is of interest. In particular, it was found out that double reduction in surface tension was achieved in distilled water at a surfactant concentration of 3.5 %, in tap water at 2 %, and in sea water at 1 %. Talking about the adsorption of TEAS, its surface excess (G) is quite simple to calculate from the data of surface tension dependence on surfactant concentration. The average molecular weight is calculated according to [21] on the TEAS composition. The results are shown in Fig.1.

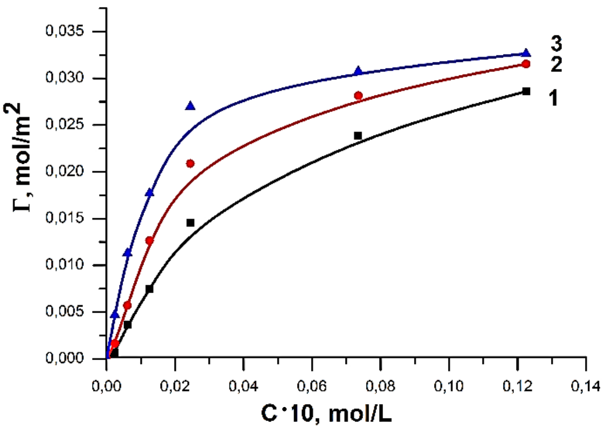

Fig. 1. TEAS adsorption isotherms 1– in distilled water; 2 – in tap water; 3 – in seawater

It can be seen that the amount of adsorption and the shape of the Γ,C-curve depends on the nature of the solvent. Adsorption from seawater solutions is closest to the Langmuir isotherm. This is confirmed by the graphs in Fig. 2, performed in the corresponding linear coordinates. The value of the adsorption limit calculated from Fig. 2 (dependence 3) is equal to 0.0365 mol / m². Unfortunately, there are no data on the size of

TEAS molecules in the literature, so it was not possible to calculate the specific surface area.

As it is shown (Fig. 1, curve 3), in seawater solutions the values of adsorption close to the limit value are achieved at lower surfactant concentrations. We can assume that this is due to the chemical nature of TEAS (R-$CH_2OSO_3N(C_2H_5)_3$), where R = C_{11} – C_{17}). It is known that due to the formation of a carbonate buffer system the pH of seawater varies in the range of 7.5 – 8.4, i.e. the medium is slightly alkaline.

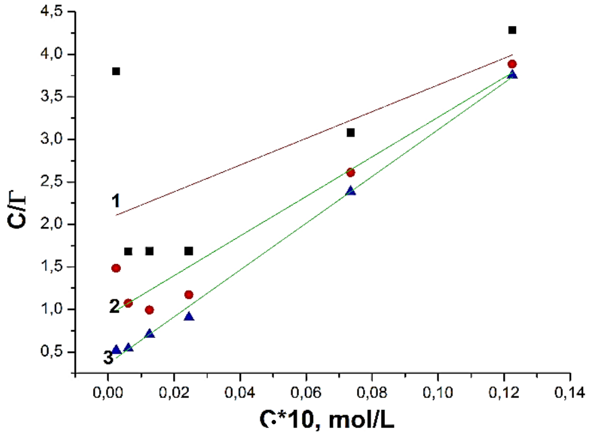

Fig. 2. TEAS adsorption in linear coordinates of the Langmuir isotherm 1– in distilled water; 2 – in tap water; 3 – in seawater

The work [22] considered the effect of sodium hydroxide concentration on the surface active properties of sodium lignosulfonate polyelectrolyte, and a conclusion about increasing polarity of its sulfo groups was made. The TEAS molecule also contains a sulfo group, and it is logical to assume that when the pH shifts to the alkaline area, its polarity and, as a result, the surface activity of the entire molecule also increases. This assumption, in particular, is confirmed by the fact that the surface activity of TEAS increases by 3.8 times when distilled water is replaced with sea water. Thus, in seawater, conditions are created for a more dense filling of the surface with a monomolecular surfactant layer compared with tap and distilled water. However, the obtained data allow determining the optimal concentration of TEAS for treating the sintering mixture for any of the solvents considered.

The increase in surface activity with increasing pH can also explain the dependence of the contact angle on the concentration of TEAS and the nature of the solvent. According to [16], the best surface wetting is observed in seawater. Since the value of the contact angle decreases continuously when surfactant concentration increases, we can conclude that TEAS moistens the sintering mixture surface with a possible transition to spreading [23].

As is well known, the best wetting of any surface corresponds to the maximum values of adhesion work. The dependence of adhesion work on the concentration of surfactant (Fig. 3), calculated from the contact angle values [16] by the formula

$$W_a = \sigma_{p.z.} \cdot (1 + \cos\theta),$$

also confirms the correctness of the choice of optimal surfactant solutions concentrations for pelletizing the sintering mixture.

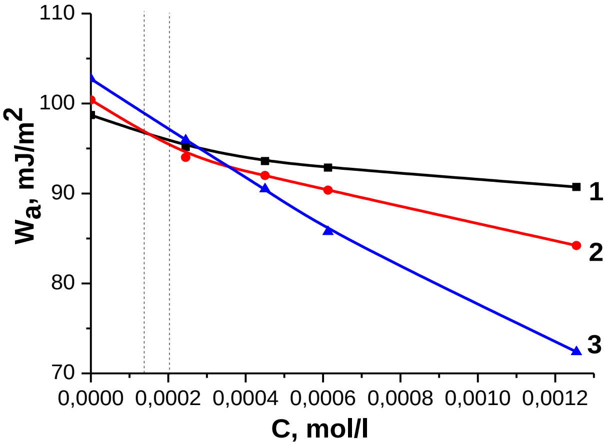

Fig. 3. Adhesion work calculated by the contact angle values depending on the TEAS concentration 1– in distilled water; 2 – in tap water; 3 – in seawater

It follows from this, that surfactant concentrations greater than optimal one for a given solvent should not significantly affect surface wettability and adhesion. However, experimental data show a different kind of dependence.

The results of bench tests according to the original method [16] show that the dependence of the force expended on rupturing bulk material from the surfactant concentration in the solution used for pelletizing (Fig. 4) has an extreme character.

This can be explained from two points of view. First, the proposed method for measuring the rupture force for bulk materials results in measuring the total effect of adhesion and cohesion forces. Consequently, when the surfactant layer on the sintering mixture surface ceases to be monomolecular, cohesion inside the specified layer is added to the adhesion force. An approximate estimate of the pelletized sintering mixture surface size according to its fractional composition showed that with a TEAS consumption of 100 g / t, more than 10 layers of molecules can be formed. And secondly, a more complete wetting of small particles with a large specific surface area can lead to an increase in the interface boundary between the sticking phases. According to [18], the separation force of multilayer disperse systems will be defined as: $F_{отр} = \pi r^2 F_1$, where F_1 is the separation force per unit of surface, and r is the particle radius.

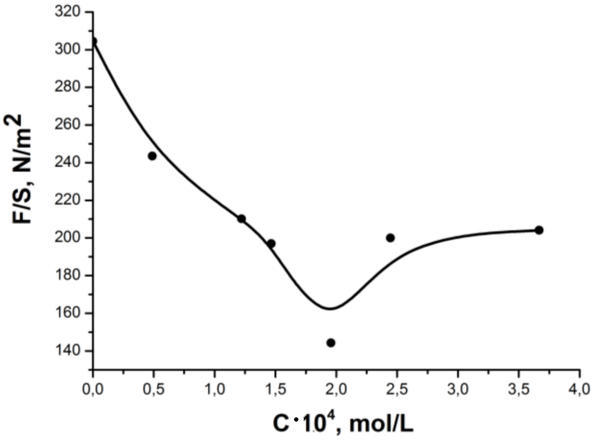

Fig. 4. The dependence of the force expended on rupturing the wetted sintering mixture on the TEAS concentration in the solution (solvent - tap water)

The dependence of the fractional composition of the pelletized sintering mixture from the surfactant consumption when wetted is a very indicative confirmation of the second assumption. The set of bench tests carried out at OJSC ArcelorMittal Krivoy Rog was designed to reveal just such a relationship [16; 19]. The fractions with particle sizes larger than 12 mm were sieved out; 12–8 mm; 8–5 mm; 5–3 mm; less than 3 mm. The smallest fractions, in fact, are a source of dustiness for the environment. Figure 5 represents the curve showing the percentage of particles larger than 3 mm in the sintering mixture, i. e. the percentage of dust-free sintering mixture, depending on the concentration of surfactants in the pelletizing solution.

As it can be seen, the maximum amount of dedusted sintering mixture falls on the same TEAS concentration values, which correspond to the minimum force expended on rupturing the moistened bulk material (Fig. 4) and acquiring the constant value of adsorption and adhesion work (Fig. 1, Fig. 3).

Of course, it is necessary to take into account the fact that in the course of pelletization volume concentration is replaced by surface concentration, and due to the complex, rough surface of sintering mixture, size effects may appear [20].

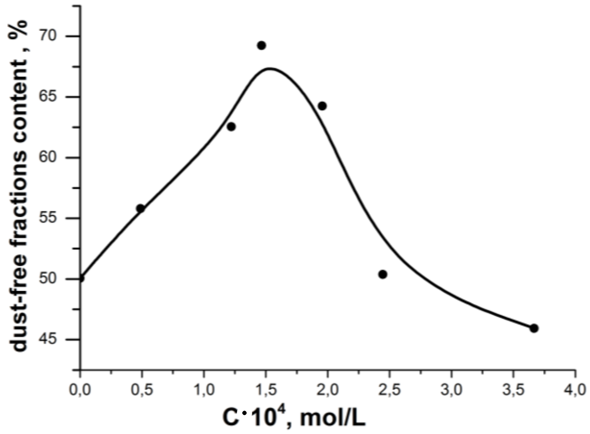

Fig. 5. The dependence of dust-free fractions content in the total weight of sintering mixture on the TEAS concentration in the pelletizing solutions (solvent - tap water).

Aside from the data from Fig. 4 and 5, this is indirectly confirmed by visual observations. Thus, at the surfactant concentration of 0.00015 – 0.00020 mol/l, which corresponded to the specific consumption of 70 – 80 g / t, fine sintering mixture had the appearance of spherical granules with sizes from 3 to 0.5 mm. But when the specific consumption amounted to more than 80 g / t, it crumbled into dust, i.e. it did not pelletize. According to [19], processing the initial sintering mixture was carried out in foam mode, and when increasing surfactant concentration, the foam strength also increased with relative constancy of the surface tension and the adsorption work value (Fig. 3). More durable, in comparison with the optimal ones, foam bubbles could “roll” off the rough surface of the particles, creating a “lotus effect”, and in the case of small particles, this effect should be more noticeable due to the smaller radius of their curvature.

The assumption that the deterioration of the mechanical properties (Fig. 4) and the change in the fractional composition (Fig. 5) of the pelletized sintering mixture is associated precisely with the deterioration of wettability is corroborated with the data [24; 25]. As it is known from [15], triethanolamine and its derivatives are absorbers of many gases. And it is logical to assume that the optimal wetting of sintering mixture – especially of small particles with developed specific surface area – will correspond to the maximum gas absorption. Dependences obtained in [15] fully fit into this assumption.

It should also be noted that at the optimum concentration of the surfactant working solution determined by us, the amount of 5–8 mm fraction, which is considered the most “useful” in the metallurgical industry, increases by 4.3 % [19], while the amount of the particles of > 10 mm fraction increases only by 1.3 %. Thus, the results obtained on the laboratory bench allow us to determine the optimal parameters for treatment of a particular kind of sintering mixture with a specific type of surfactant solutions, and the calculations allow us to expand the scope of the applied research to other surfactants and other bulk materials.

Conclusions

Based on a study of the main physicochemical characteristics of surfactant solutions (surface tension, adsorption, contact angle, adhesion work, rupture force for bulk materials, etc.) and a complex of laboratory, theoretical and bench studies of sintering mixture treatment with surfactant solutions, the optimal parameters of this process were established. The optimal surfactant concentration in the pelletizing solution is 0.00015 – 0.00020 mol/l at a flow rate of 70 – 80 g per ton of sintering mixture; the best wetting is achieved in seawater. It is noted that not only a decrease, but also an increase in the TEAS concentration relative to the optimal value leads to a noticeable deterioration in the sintering mixture quality. This may be due to the deterioration of the surface wettability on account of size effects. When changing the solvent from distilled water to seawater, it appears to be polarization of surfactant sulfo group, which leads to a significant (in 3.5 times) increase in the surface activity of diphilic molecules.

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